

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-313057

(P2001-313057A)

(43) 公開日 平成13年11月9日 (2001.11.9)

| (51) Int.Cl. ⁷ | 識別記号 | F I | テームコード* (参考) |
|-------------------------------------|-------|---------------|-----------------|
| H 0 1 M 8/06 | | H 0 1 M 8/06 | R 4 D 0 0 6 |
| B 0 1 D 69/02 | | B 0 1 D 69/02 | 4 F 0 0 6 |
| 71/26 | | 71/26 | 4 F 0 7 1 |
| 71/32 | | 71/32 | 4 F 0 7 3 |
| C 0 8 J 5/22 | C E Z | C 0 8 J 5/22 | C E Z 4 L 0 3 1 |
| 審査請求 未請求 請求項の数 4 O L (全 6 頁) 最終頁に続く | | | |

(21) 出願番号 特願2000-127406 (P2000-127406)

(22) 出願日 平成12年4月27日 (2000.4.27)

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(54) 【発明の名称】 固体高分子型燃料電池用イオン交換性フィルタの製造方法

(57) 【要約】

【課題】 アノード及びカソードに供給されるガス中に含まれる不純物を除去するための耐久性に優れるイオン交換性フィルタを提供し、固体高分子型燃料電池セル内に外部から混入する不純物を減少させ、長期的に性能を安定させる。

【解決手段】 ポリオレフィン又はポリフルオロオレフィンからなる基材フィルタを表面親水化処理した後、該基材フィルタにイオン交換性ポリマー溶液を塗布し、乾燥してイオン交換性フィルタを得る。

【特許請求の範囲】

【請求項 1】イオン交換膜からなる電解質膜と該電解質膜を介して対向するアノードとカソードを備える固体高分子型燃料電池に供給される水素を含むガス又は酸素を含むガスを清浄にするためのイオン交換性フィルタの製造方法であって、ポリオレフィン又はポリフルオロオレフィンからなる基材フィルタを表面親水化処理した後、該基材フィルタにイオン交換性ポリマー溶液を塗布し、乾燥することを特徴とする固体高分子型燃料電池用イオン交換性フィルタの製造方法。

【請求項 2】前記基材フィルタは、厚さ 10～5000 μm 、目付量 5～2500 g/m^2 である請求項 1 に記載のイオン交換性フィルタの製造方法。

【請求項 3】前記基材フィルタは、放射線処理、放電処理、薬品処理及びグラフト重合処理からなる群から選ばれた 1 種以上の処理により表面親水化処理される請求項 1 又は 2 に記載のイオン交換性フィルタの製造方法。

【請求項 4】イオン交換膜からなる電解質膜と該電解質膜を介して対向するアノードとカソードを備え、アノードには水素を含むガスが、カソードには酸素を含むガスが供給され、前記水素を含むガス及び／又は前記酸素を含むガスはイオン交換性フィルタを通して供給される固体高分子型燃料電池の製造方法において、前記イオン交換性フィルタは、ポリオレフィン又はポリフルオロオレフィンからなる基材フィルタを表面親水化処理した後、イオン交換性ポリマー溶液を塗布し乾燥することにより得ることを特徴とする固体高分子型燃料電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は固体高分子型燃料電池に供給されるガスを清浄にするためのイオン交換性フィルタに関する。

【0002】

【従来の技術】現在使用されている固体高分子型燃料電池は、長期間使用すると発電電圧が低下する等、電池性能安定性に問題がある。この原因の 1 つに使用する気体からの不純物の混入があり、特にイオン性物質が混入すると使用されている固体高分子電解質膜の抵抗が増大し、性能安定性が低下する。

【0003】従来、空気等のガスを浄化するために、主に気体中の微粒子を除去する目的で HEPA フィルタ (High Efficiency Particulate Air Filter) や ULPA フィルタ (Ultra Low Penetration Air Filter) が用いられている。しかし、HEPA フィルタは気体状不純物を分離できないので、ガス中に酸性ガスやアルカリ性ガス等の気体不純物が含まれている場合には、酸、アルカリ、過マンガン酸カリウム等を付着させた活性炭フィルタを利用することが多かった。こ

の場合には活性炭に薬品を付着させる操作が煩雑で、しかも付着物が流出するおそれがあり、中和によって生成した塩が飛散することもあった。

【0004】このような問題を解決するために、ポリエチレン等の繊維にモノマーをグラフト重合したイオン交換繊維でフィルタを作製し、該フィルタをエアフィルタに使用することが「空気清浄」第 36 巻第 3 号 34 ページに記載されている。また、ポリプロピレンが島成分でポリスチレンが海成分の多芯海島型複合繊維のポリスチレン部分にイオン交換基を導入したイオン交換繊維でフィルタを作製しエアフィルタに使用した例が「多孔質体の性質とその応用技術」(フジテクノシステム) 747 ページに記載されている。

【0005】

【発明が解決しようとする課題】しかし、これらのイオン交換繊維は合成が煩雑なうえ、スチレンモノマーをベースとしているものが多いため繊維が剛直で脆性が強く、長期間使用すると破損しやすく耐久性が劣る問題があった。

【0006】そこで本発明は、アノード及びカソードに供給されるガス中に含まれる不純物を除去するための耐久性に優れたイオン交換性フィルタを提供し、固体高分子型燃料電池セル内に外部から混入する不純物を減少させ、長期的に性能が安定した固体高分子型燃料電池を提供することを目的とする。

【0007】

【課題を解決するための手段】本発明は、イオン交換膜からなる電解質膜と該電解質膜を介して対向するアノードとカソードを備える固体高分子型燃料電池に供給される水素を含むガス又は酸素を含むガスを清浄にするためのイオン交換性フィルタの製造方法であって、ポリオレフィン又はポリフルオロオレフィンからなる基材フィルタを表面親水化処理した後、該基材フィルタにイオン交換性ポリマー溶液を塗布し、乾燥することを特徴とする固体高分子型燃料電池用イオン交換性フィルタの製造方法を提供する。

【0008】

【発明の実施の形態】本発明のイオン交換性フィルタは、基材フィルタがポリオレフィン又はポリフルオロオレフィンからなる。ポリオレフィン又はポリフルオロオレフィンを使用すると、強度や化学的安定性、耐久性の面で好ましい。しかし、ポリオレフィンやポリフルオロオレフィンは表面に親水性官能基がなく撥水性であり、イオン交換ポリマー等の親水性ポリマーとの接着性が良好でない。したがって、ポリオレフィン又はポリフルオロオレフィンからなる基材フィルタを表面処理して表面に親水性官能基を導入した後に、イオン交換ポリマー溶液を塗布することが接着性向上の観点から好ましく、本発明ではこの方法を採用している。したがって、本発明における基材フィルタの表面親水化処理とは、基材フィ

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ルタに親水性官能基を導入するための表面処理を示している。

【0009】本発明における基材フィルタは、厚さ10～5000 μ m、目付量5～2500g/m²であることが好ましい。厚さが10 μ mより薄い場合又は目付量が5g/m²より小さい場合には取り扱いにくく、またフィルタの強度が低い場合フィルタが加工中に破損しやすい。厚さが5000 μ mより厚い場合又は目付量が2500g/m²より大きい場合には塗布乾燥の工程に時間がかかり、また得られるフィルタの圧損も大きくなるので好ましくない。厚さが100～1000 μ m、目付量が50～500g/m²である場合には強度が高く、圧損も少ないので特に好ましい。

【0010】本発明において基材フィルタを表面親水化処理する方法としては、放射線処理、放電処理、薬品処理又はグラフト重合処理等が挙げられる。基材フィルタにこれらの処理が施されると、イオン交換性ポリマーと基材との接着性が向上し、耐久性に優れるイオン交換性フィルタが得られる。

【0011】放射線処理の方法としては、 γ 線や電子線が用いられる。放射線の照射線量は1～200kGy、特に10～100kGyが好ましい。照射線量が1kGyより小さいと表面親水化処理効果が小さく、また200kGyより大きいと基材を構成するポリマーの分子鎖の切断が進行し、基材フィルタ繊維自体の強度が低下するおそれがある。照射線量が1～200kGyの場合には基材フィルタ繊維の強度低下は著しくなく、カルボン酸基や水酸基等の官能基やラジカル等、イオン交換性ポリマーとの接着性を向上させる活性種が基材に効率的に導入される。

【0012】放電処理の方法としては、常圧下でのコロナ放電処理や減圧下でのプラズマ放電処理が挙げられる。コロナ放電の処理条件としては、出力が1～3kW、処理速度が3～30m/分であることが好ましい。出力が1kWより小さいと放電できず、また3kWより大きいと発熱量が大きくなり基材の強度が低下する。処理速度が3m/分より遅いと、処理が過度に行われるため基材の強度が低下するおそれがあり、30m/分より速いと十分に処理できないおそれがある。

【0013】プラズマ放電の処理条件としては、圧力5～100Paの空気、酸素、アルゴン等の気体の存在下で、出力0.01～0.5kW、処理速度0.01～5m/分で処理するのが好ましい。圧力が5Paより低かったり100Paより高いと放電できない。使用する気体は特に限定されないが、カルボン酸基や水酸基等の官能基を基材に導入するためには酸素を含む気体が好ましい。またアルゴンはプラズマを安定させる効果があるので好ましい。気体は単独で用いてもよいが2種以上の気体を混合して用いてもよい。

【0014】出力が0.01kWより低いと処理効果が

小さく、また0.5kWより高いと発熱が大きく基材の強度が低下する。処理速度は0.01m/分より遅いと処理が過度となり基材の強度が低下し、また5m/分より速いと十分に処理できないおそれがある。

【0015】薬品処理の方法としては、クロロスルホン酸、硫酸、発煙硫酸、発煙硫酸/リン酸トリエチル錯体等に基材フィルタを浸漬する方法が挙げられる。なかでもクロロスルホン酸を使用すると、低温でも効率的にスルホンクロリド基を基材フィルタに導入できるため好ましい。クロロスルホン酸を用いる場合は、そのまま用いてもよいが、基材の官能基導入反応に伴う強度低下を制御するために、テトラクロロエタンやトリクロロエタン等の溶媒で10～50質量%程度に希釈して使用することが好ましい。

【0016】放射線グラフト重合法による処理方法としては、基材フィルタに官能基を含有するモノマー又は官能基を導入可能なモノマー（以下、まとめて官能基導入モノマーという）を浸漬させながら放射線照射しグラフト重合させてもよいし、基材フィルタに放射線を照射した後に官能基導入モノマーを浸漬させてグラフト重合させてもよい。しかし、基材フィルタに官能基導入モノマーを浸漬させながら放射線照射する方法は取り扱いが煩雑であるので、後者の方法が好ましい。

【0017】放射線グラフト重合法における放射線処理は、上述した放射線処理と同様の条件にての処理が好ましい。さらにここでの放射線照射は、照射中に発生するラジカルを保護するため、減圧下又は窒素等の不活性ガス雰囲気中で行うことが好ましい。また、放射線を照射してから基材を官能基導入モノマーに浸漬するまでの間は、ラジカル濃度の低下を防ぐために基材を低温で保持することが好ましい。基材の官能基導入モノマーへの浸漬も、減圧下又は不活性ガス雰囲気中で行うことが好ましく、グラフト重合の温度は40～90℃が好ましい。

【0018】官能基導入モノマーとしては、スチレン、 α -メチルスチレン、クロロメチルスチレン、アルキルメタクリレート、アルキルアクリレート、アクリロニトリル、アクロレイン、グリシジルメタクリレート、グリシジルアクリレート、ビニルアセテート、スチレンスルホン酸又はその塩、アクリル酸又はその塩、メタクリル酸又はその塩、クロトン酸、イタコン酸、2-アクリルアミド-2-メチルプロパンスルホン酸、パーフルオロスルホンフルオリド、ビニルベンジルトリメチルアンモニウムクロリド、アリアルアミン又はその塩、4-ビニルピリジン、2-ビニルピリジン、1-ビニルイミダゾール、2-ビニルピラジン、4-(3-ブテンリ)ピリジン、アクリルアミド、N,N-ジメチルアクリルアミド、N-(3-(N,N-ジメチル)アミノプロピル)アクリルアミド、2-(N,N-ジメチルアミノエチル)アクリレート、2-ヒドロキシエチルアクリレート、2-ヒドロキシエチルメタクリレート、ビニル基と

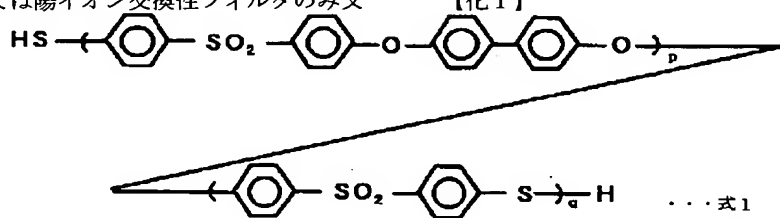
スルホン酸基を有する化合物又はその塩、 $\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2-\text{CF}(\text{CF}_3))_v-(\text{CF}_2)_w-\text{COOCH}_3$ 等で表されるメトキシカルボニル基を有する含フッ素化合物（ただし、 v, w は0以上の整数であり、 $v=w=0$ ではない。）等が挙げられる。

【0019】上記官能基導入モノマーは液体である場合は基材フィルタを直接浸漬してもよいし、溶媒を用いて希釈してから基材フィルタを浸漬してもよい。また、基材フィルタを官能基導入モノマーに浸漬する方法以外に、減圧下で官能基導入モノマーを気体にして基材フィルタに導入する方法も採用でき、この場合は窒素等の不活性ガスで気体を希釈することもできる。官能基導入モノマーが固体である場合は、官能基導入モノマーが溶解する溶媒に溶解させて使用できる。

【0020】上記の放射線処理、放電処理、薬品処理及びグラフト重合法処理は、いずれか1種の処理を行ってもよいし、2種以上の処理を併用してもよい。

【0021】本発明で使用するイオン交換性ポリマーのイオン交換容量は0.8~4.0ミリ当量/g乾燥樹脂であることが好ましい。イオン交換容量が0.8ミリ当量/g乾燥樹脂より小さいとガス中の不純物であるイオン性物質を十分に除去するために使用するイオン交換性ポリマーが大量に必要となり、装置が大きくなるので好ましくない。また、イオン交換容量が4.0ミリ当量/g乾燥樹脂より大きいとイオン交換性ポリマーの強度が低下して処理中に破損が起こりやすい。イオン交換容量が1.0~3.0ミリ当量/g乾燥樹脂である場合には、イオン交換性ポリマーの強度もあり、効率的にガスを処理できるので特に好ましい。

【0022】本発明において、燃料電池に供給されるガスは、不純物によっては陽イオン交換性フィルタのみ又



【0026】次に、750gの共重合体aを10Lの1, 1, 2, 2-テトラクロロエタンに溶解した後、4000gの（クロロメトキシ）メタン及び45gの無水塩化スズを添加し、110℃にて4時間クロロメチル化反応を行った。次いで、メタノール50Lを用いて反応生成物を沈殿させた後、該反応生成物を洗浄し、共重合体aをクロロメチル化した共重合体（以下、共重合体bという）850gを得た。共重合体bにおけるクロロメチル基の導入率は、1繰り返し単位あたり約1.9個であり、このクロロメチル基をすべてトリメチルアミンによりアミノ化したところ、イオン交換容量は2.2ミリ当量/g乾燥樹脂であった。

は陰イオン交換性フィルタのみを通過させてから供給されてもよいが、陽イオン交換性フィルタと陰イオン交換性フィルタの両方を通過させてから供給されることが好ましい。この場合、例えば陽イオン交換性ポリマーを用いて作製した陽イオン交換性フィルタと陰イオン交換性ポリマーを用いて作製した陰イオン交換性フィルタとを積層し、ガスが両方のイオン交換性フィルタを通過してから燃料電池に供給されるようにすればよい。

【0023】

【実施例】〔例1〕特開昭61-168629の実施例11に記載された合成法に準じて、以下のようにして式1で表されるポリスルホン/ポリチオエーテルスルホン共重合体（以下、共重合体aという）を得た。

【0024】まず、オートクレーブに3.6モルのビスフェノールAと、水酸化ナトリウム水溶液、N-メチル-2-ピロリドン及びトルエンを仕込み、窒素ガスを流しながら加熱して水及びトルエンを除去し冷却した。これに3.96モルの4, 4'-ジクロロジフェニルスルホン（以下、ジクロロジフェニルスルホン）を仕込み、窒素雰囲気中で160℃で3時間反応させ、芳香族ポリスルホンの繰り返し単位からなる反応物を得た。冷却後、これに3.24モルのジクロロジフェニルスルホンと、3.78モルの硫化ナトリウムと、無水酢酸リチウム及びN-メチル-2-ピロリドンを加えて窒素ガスで0.49MPaに加圧し160℃にて3時間反応させ、2200gの共重合体aを得た。なお、式1において $p/q=1/1$ であり、共重合体aの固有粘度は0.50であった。また、電子吸引性基である $-\text{SO}_2-$ と結合していない芳香族環の含有率は、共重合体aの全芳香族環中で33モル%であった。

【0025】

【化1】

【0027】500gの共重合体bを2830gのN,N-ジメチルホルムアミドに溶解し、得られた溶液を0℃にて攪拌しながら、1モル/LのトリメチルアミンのN,N-ジメチルホルムアミド溶液1140mLをゆっくり滴下した。次いでこれに2-メトキシエタノール500gを添加し、イオン交換容量2.0ミリ当量/g乾燥樹脂の陰イオン交換ポリマーの溶液を得た。

【0028】また、500gの共重合体aを3350mLの1, 1, 2-トリクロロエタンに溶解した溶液と、281gのリン酸トリエチルと2000mLの1, 1, 2-トリクロロエタンとの混合液に0℃にて60%発煙硫酸412gを滴下混合した溶液との2種の溶液を準備

し、この2種の溶液を1, 1, 2-トリクロロエタン3500 mL中に25℃で滴下した。これを100時間攪拌し、析出ポリマーをろ過、洗浄、乾燥してスルホン酸基が導入された陽イオン交換ポリマー420 gを得た。得られたポリマーにおけるスルホン酸基の導入率は、1繰り返し単位あたり約1.5個であり、イオン交換容量は2.0ミリ当量/g乾燥樹脂であった。得られたポリマー400 gをN-メチル-2-ピロリドン1600 gに溶解し陽イオン交換ポリマー溶液を得た。

【0029】厚さ500 μm 、目付量200 g/ m^2 のポリエチレン繊維からなるフィルタを減圧下にて10 kGy/hの照射速度で5時間、合計で50 kGyの γ 線照射を行ったものを2枚用意し、上記の各溶液に浸漬、乾燥し陰イオン交換性フィルタ及び陽イオン交換性フィルタを作製した。乾燥後のフィルタの厚さはそれぞれ510 μm 及び530 μm であり、目付量は285 g/ m^2 及び300 g/ m^2 であった。陰イオン交換性フィルタについては0.1モル/Lの水酸化ナトリウム水溶液に浸漬させて対イオンがOHイオンの4級アンモニウム塩基とした。

【0030】得られた陽イオン交換性フィルタ及び陰イオン交換性フィルタをそれぞれ直径10 cmの円盤状に切り、2枚重ねてフィルタホルダに収容し、カソード側の空気を供給するコンプレッサと燃料電池セルの間に設置し、カソード側空気はこのフィルタを通過したものが燃料電池セルに供給されるようにした。

【0031】燃料電池セルは以下のようにして組み立てた。テトラフルオロエチレンに基づく重合単位と $\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ に基づく重合単位とからなる共重合体(イオン交換容量1.1ミリ当量/g乾燥樹脂)と白金担持カーボンとを1:3の質量比で含み、エタノールを溶媒とする塗工液を、カーボン布上にダイコート法で塗工した。これを乾燥して厚さ10 μm 、白金担持量0.5 mg/ cm^2 のガス拡散電極層が形成されたガス拡散電極を作製した。

【0032】上記ガス拡散電極2枚の間に、テトラフルオロエチレンに基づく重合単位と $\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$ に基づく重合単位とからなる共重合体(イオン交換容量1.1ミリ当量/g乾燥樹脂)からなる陽イオン交換膜(厚さ50 μm)を挟み、平板プレス機を用いてプレスして膜電極接合体を作製した。この膜電極接合体の外側にチタン製の集電体、さらにその外側にPTFE製のガス供給室、さらにその外側にヒーターを配置し、有効膜面積9 cm^2 の燃料電池セルを組み立てた。

【0033】燃料電池の温度を80℃に保ち、カソードにフィルタを通過した空気、アノードに水素をそれぞれ2気圧で供給した。電流密度1 A/ cm^2 のときの端子電圧を測定したところ、端子電圧は0.60 Vであった。さらに、上記の燃料電池を80℃、電流密度1 A/

cm^2 で連続運転を行った。1000時間後の端子電圧は0.60 Vであり初期と変化がなかった。

【0034】[例2]ポリスルホンの共重合体(アモコ社製、商品名:ユーデルP-1700)500 gを1, 1, 2, 2-テトラクロロエタン5200 mLに溶解した後、(クロロメトキシ)メタン2350 g、無水塩化スズ45 gを添加して、窒素パージしながら温度50℃にて0.5時間クロロメチル化反応を行った。次いで、メタノール40 Lにて反応生成物を沈殿させた後、該反応生成物を洗浄し、クロロメチル化共重合体(以下、共重合体cという)530 gを得た。共重合体cにおけるクロロメチル基の導入率は、1繰り返し単位に約0.9個であり、このクロロメチル基をすべてトリメチルアミンでアミノ化したところ、イオン交換容量は1.7ミリ当量/g乾燥樹脂であった。

【0035】500 gの共重合体cをN, N-ジメチルホルムアミド2830 gに溶解して15質量%溶液を調製した。この溶液を0℃にて攪拌しながら、1モル/LのトリメチルアミンのN, N-ジメチルホルムアミド溶液の470 mLをゆっくり滴下した後、2-メトキシエタノール70 gを添加し、イオン交換容量が0.9ミリ当量/g乾燥樹脂の陰イオン交換性ポリマー溶液を得た。

【0036】一方、アゾビスイソブチロニトリルを開始剤として、2モルのテトラフルオロエチレンと0.45モルの $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ とを、70℃にて5時間共重合し、イオン交換容量1.1ミリ当量/g乾燥樹脂の共重合体を得た。これを20% KOH水溶液中で90℃にて16時間かけて加水分解した後、1モル/Lの塩酸に室温にて16時間浸漬して SO_2F 基を酸型に変換し、水洗乾燥後エタノールに溶解することにより、スルホン酸基を有するパーフルオロカーボン重合体を溶液全質量の9%含む陽イオン交換性ポリマー溶液を得た。

【0037】厚さ500 μm 、目付量200 g/ m^2 のポリエチレン繊維からなるフィルタを出力2 kW、処理速度5 m/分でコロナ放電処理したものを2枚用意し、それぞれ上記の各溶液に浸漬し、乾燥して陰イオン交換性フィルタ及び陽イオン交換性フィルタを作製した。乾燥後のフィルタの厚さはそれぞれ530 μm 及び540 μm であり、目付量は300 g/ m^2 及び310 g/ m^2 であった。陰イオン交換性フィルタについては0.1モル/L水酸化ナトリウム水溶液に浸漬させて対イオンがOHイオンの4級アンモニウム塩基とした。

【0038】例1と同様にして燃料電池セルを組み立て評価を行った。燃料電池の温度を80℃に保ち、カソードにフィルタを通過した空気、アノードに水素をそれぞれ2気圧で供給した。電流密度1 A/ cm^2 のときの端子電圧を測定したところ、端子電圧は0.58 Vであった。さらに、上記の燃料電池セルを80℃、電流密度1

A/cm²で連続運転を行った。1000時間後の端子電圧は0.58Vであり初期と変化がなかった。

【0039】[例3(比較例)]例1において、フィルタホルダにポリエチレン繊維製フィルタを処理せずに2枚重ねてセットした以外は例1と同様にして燃料電池セルを組み立て、評価した。電流密度1A/cm²のときの端子電圧を測定したところ、端子電圧は0.60Vであった。しかし、1000時間運転後の端子電圧は0.51Vに低下した。

【0040】[例4(比較例)]例2において、ポリエチレン繊維製フィルタをコロナ放電処理せずに各イオン交換性ポリマー溶液に浸漬、乾燥し陰イオン交換性フィルタ及び陽イオン交換性フィルタを作製した。乾燥後のフィルタの厚さはそれぞれ530μm及び540μmであり、目付量は300g/m²及び310g/m²あつ

た。陰イオン交換性フィルタについては0.1mol/Lの水酸化ナトリウム水溶液に浸漬させて対イオンがOHイオンの4級アンモニウム塩基とした。例2と同様にしてフィルタホルダに得られたフィルタを2枚重ねてセットした以外は同様にして燃料電池セルを組み立て、評価した。電流密度1A/cm²のときの端子電圧を測定したところ、端子電圧は0.59Vであった。しかし、1000時間運転後の端子電圧は0.53Vに低下した。

【0041】

【発明の効果】本発明では、耐久性に優れるイオン交換性フィルタによって処理したガス、すなわちイオン成分が除去されたガスを固体高分子型燃料電池に供給しているので、固体高分子電解質膜内へのイオンの蓄積がなくなる。そのため、燃料電池を長期間作動させても、抵抗の上昇を抑制でき発電電圧の低下を抑制できる。

フロントページの続き

| (51)Int.Cl. ⁷ | | 識別記号 | F I | テーマコード(参考) | |
|--------------------------|-------|-------|---------|------------|-----------------|
| C 08 J | 7/00 | 3 0 2 | C 08 J | 7/00 | 3 0 2 4 L 0 3 3 |
| | 7/04 | | | 7/04 | Z 5 H 0 2 6 |
| D 0 6 M | 10/00 | | D 0 6 M | 10/00 | J 5 H 0 2 7 |
| | 10/02 | | | 10/02 | B |
| | 11/52 | | | 14/10 | |
| | 14/10 | | | 14/12 | |
| | 14/12 | | H 0 1 M | 8/10 | |
| H 0 1 M | 8/10 | | C 0 8 L | 81:06 | |
| // C 0 8 L | 81:06 | | D 0 6 M | 7/02 | A |

Fターム(参考) 4D006 GA41 MA03 MA06 MA11 MA13
 MA14 MA31 MA40 MB04 MB09
 MB17 MC22 MC28 MC30X
 MC62X MC74X MC75 MC78X
 MC82 NA03 NA10 NA12 NA42
 NA46 NA54 NA58 NA63 NA64
 PA01 PB62 PB66 PC80
 4F006 AA12 AA18 AB32 BA01 CA08
 DA04
 4F071 AA14C AA26C AA62X AA64X
 AH12 FB03 FC01 FC02 FC04
 FC06 FC07 FD03
 4F073 AA01 BA06 BA15 BB01 CA41
 EA01 EA32 EA37
 4L031 BA12 CB06 CB08 DA00 DA08
 4L033 AC07 AC15 CA58 CA70 DA01
 5H026 AA06
 5H027 AA06

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-313057

(43)Date of publication of application : 09.11.2001

(51)Int.Cl. H01M 8/06
B01D 69/02
B01D 71/26
B01D 71/32
C08J 5/22
C08J 7/00
C08J 7/04
D06M 10/00
D06M 10/02
D06M 11/52
D06M 14/10
D06M 14/12
H01M 8/10
// C08L 81:06

(21)Application number : 2000-127406

(71)Applicant : ASAHI GLASS CO LTD

(22)Date of filing : 27.04.2000

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(54) MANUFACTURING METHOD OF ION-EXCHANGE FILTER FOR SOLID POLYMER FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ion-exchange filter which is good at durability for eliminating impurities contained in gas supplied to an anode and a cathode, reduce the impurities mixing into the inside a solid polymer fuel cell from outside, and stabilize its performance for a long period of time.

SOLUTION: The ion-exchange filter is obtained by processing hydrophilic surface treatment of a base material filter made up of polyolefin or polyfluorolefin, applying ion-exchange polymer solution on the filter, and then by drying it.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the ion-exchange nature filter for polymer electrolyte fuel cells which applies an ion-exchange nature polymer solution to this base material filter, and is characterized by to dry after carrying out the surface hydrophilization processing of the base material filter which is the manufacture approach of the ion-exchange nature filter for making into clarification the gas containing the gas containing the hydrogen supplied to the anode which counters through the electrolyte membrane and this electrolyte membrane which consists of ion exchange membrane, and a polymer electrolyte fuel cell equipped with a cathode, or oxygen, and consists of polyolefine or a poly fluoro olefin.

[Claim 2] Said base material filter is the manufacture approach of the ion-exchange nature filter according to claim 1 which are 10-5000 micrometers in thickness, metsuke amount 5-2500g/m2.

[Claim 3] Said base material filter is the manufacture approach of the ion-exchange nature filter according to claim 1 or 2 in which surface hydrophilization processing is carried out by one or more sorts of processings chosen from the group which consists of radiation treatment, electrodischarge treatment, a chemical treatment, and graft polymerization method processing.

[Claim 4] It has the anode and cathode which counter through the electrolyte membrane and this electrolyte membrane which consist of ion exchange membrane. In the manufacture approach of a polymer electrolyte fuel cell that the gas by which the gas which contains hydrogen in an anode contains oxygen in a cathode is supplied, and the gas containing the gas containing said hydrogen and/or said oxygen is supplied through an ion-exchange nature filter Said ion-exchange nature filter is the manufacture approach of the polymer electrolyte fuel cell characterized by obtaining by applying an ion-exchange nature polymer solution and drying after carrying out surface hydrophilization processing of the base material filter which consists of polyolefine or a poly fluoro olefin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ion-exchange nature filter for making into clarification the gas supplied to a polymer electrolyte fuel cell.

[0002]

[Description of the Prior Art] When the polymer electrolyte fuel cell used now is used for a long period of time, a problem is in cell engine-performance stability -- a generation-of-electrical-energy electrical potential difference falls. Resistance of the solid-state polyelectrolyte film currently used if there is mixing of the impurity from the gas used for one of the cause of this and especially the ionicity matter mixes increases, and engine-performance stability falls.

[0003] The HEPA filter (High Efficiency Particulate Air Filter) and the ULPA filter (Ultra Low Penetration Air Filter) are used in order to purify gas, such as air, conventionally, and to mainly remove the particle in a gas. However, since the HEPA filter could not separate a gas-like impurity, when gas impurities, such as a sour gas and alkaline gas, were contained in gas, the charcoal filter to which an acid, alkali, potassium permanganate, etc. were made to adhere was used in many cases. In this case, actuation of making a chemical adhering to activated carbon is complicated, there is a possibility that an affix may moreover flow out, and the salt generated by neutralization might disperse.

[0004] producing a filter for the ion-exchange fiber which carried out the graft polymerization of the monomer to fiber, such as polyethylene, and using this filter for an air filter, in order to solve such a problem -- "air clarification" -- it is indicated by the 36th volume No. 3 34 pages. Moreover, the example which polypropylene produced the filter for the ion-exchange fiber to which polystyrene introduced the ion exchange group into the polystyrene part of the multicore sea-island type bicomponent fiber of a sea component of the island component, and used for the air filter is indicated by "property and applied-technology of porous body" (FUJITEKUNO system) 747 page.

[0005]

[Problem(s) to be Solved by the Invention] However, these ion-exchange fiber had the problem in which endurance is [that it will be easy to damage if fiber is upright, and brittleness is strong and uses it for a long period of time, since there is much what is using the styrene monomer as the base] inferior the top where composition is complicated.

[0006] Then, this invention offers the ion-exchange nature filter which is excellent in the endurance for removing the impurity contained in the gas supplied to an anode and a cathode, decreases the impurity mixed from the outside in a polymer electrolyte fuel cell cel, and aims at offering the polymer electrolyte fuel cell whose engine performance was stable in the long run.

[0007]

[Means for Solving the Problem] This invention is the manufacture approach of the ion-exchange nature filter for making into clarification the gas containing the hydrogen supplied to the anode which counters through the electrolyte membrane and this electrolyte membrane which consist of ion exchange membrane, and a polymer electrolyte fuel cell equipped with a cathode, or oxygen. After carrying out surface hydrophilization processing of the base material filter which consists of polyolefine or a poly fluoro olefin, the manufacture approach of the ion-exchange nature filter for polymer electrolyte fuel cells which applies an ion-exchange nature polymer solution to this base material filter, and is characterized by drying is offered.

[0008]

[Embodiment of the Invention] As for the ion-exchange nature filter of this invention, a base material filter

consists of polyolefine or a poly fluoro olefin. When polyolefine or the poly fluoro olefin is used, it is desirable in respect of reinforcement, or chemical stability and endurance. However, neither polyolefine nor the poly fluoro olefin has a hydrophilic functional group in a front face, and is water repellence, and its adhesive property with hydrophilic polymers, such as an ion-exchange polymer, is not good. Therefore, after carrying out surface treatment of the base material filter which consists of polyolefine or a poly fluoro olefin and introducing a hydrophilic functional group into a front face, it is desirable from a viewpoint of adhesive improvement to apply an ion-exchange polymer solution, and it has adopted this approach in this invention. Therefore, surface hydrophilization processing of the base material filter in this invention shows the surface treatment for introducing a hydrophilic functional group to the base material filter.

[0009] As for the base material filter in this invention, it is desirable that they are 10-5000 micrometers in thickness, metsuke amount 5 - 2500 g/m². When thickness is thinner than 10 micrometers, or when metsuke amount is smaller than 5 g/m², it is hard to deal with it, and since the reinforcement of a filter is low, it is easy to damage while a filter processes it. Since the process of spreading desiccation takes time amount and the pressure loss of the filter obtained also becomes large when thickness is thicker than 5000 micrometers, or when metsuke amount is larger than 2500 g/m², it is not desirable. When thickness is 100-1000 micrometers and metsuke amount is 50 - 500 g/m², reinforcement is high, and especially since there are also few pressure losses, it is desirable.

[0010] As an approach of carrying out surface hydrophilization processing of the base material filter in this invention, radiation treatment, electrodischarge treatment, a chemical treatment, or graft polymerization method processing is mentioned. If these processings are performed to a base material filter, the adhesive property of an ion-exchange nature polymer and a base material will improve, and the ion-exchange nature filter which is excellent in endurance will be obtained.

[0011] A gamma ray and an electron ray are used as the approach of radiation treatment. Especially the quantity of radiation of a radiation has desirable 10-100kGy one to 200 kGy. If larger [when quantity of radiation is smaller than 1kGy, a surface hydrophilization treatment effect is small, and] than 200kG(ies), cutting of the chain of the polymer which constitutes a base material will advance, and there is a possibility that the reinforcement of base material filter fiber itself may fall. When quantity of radiation is 1-200kGy, the active species in which the fall of base material filter fiber on the strength raises an adhesive property with an ion-exchange nature polymer as for functional groups, radicals, etc., such as a carboxylic-acid radical and a hydroxyl group, and deals remarkably is efficiently introduced into a base material.

[0012] As the approach of electrodischarge treatment, the corona discharge treatment under ordinary pressure and the plasma electrodischarge treatment under reduced pressure are mentioned. As processing conditions for corona discharge, it is desirable that an output is 1-3kW and processing speed is a part for 3-30m/. If an output is smaller than 1kW, it cannot discharge, and if larger than 3kW, calorific value will become large, and the reinforcement of a base material falls. There is a possibility that the reinforcement of a base material may fall since processing is performed too much if processing speed is slower than a part for 3m/, and when quicker than a part for 30m/, there is a possibility that it cannot fully process.

[0013] As processing conditions for plasma discharge, it is desirable under existence of gases, such as air, oxygen, and an argon, with a pressure of 5-100Pa to process by part for output [of 0.01-0.5kW] and processing speed/of 0.01-5m. A pressure cannot be lower than 5Pa, or if higher than 100Pa, it cannot discharge. Although especially the gas to be used is not limited, in order to introduce functional groups, such as a carboxylic-acid radical and a hydroxyl group, into a base material, the gas containing oxygen is desirable. Moreover, since an argon is effective in stabilizing the plasma, it is desirable. Although a gas may be used independently, it may mix and use two or more sorts of gases.

[0014] If higher [when an output is lower than 0.01kW, a treatment effect is small, and] than 0.5kW, generation of heat will be large and the reinforcement of a base material will fall. If later than a part for 0.01m/, processing will become excessive, the reinforcement of a base material will fall, and when processing speed is quicker than a part for 5m/, it has a possibility that it cannot fully process.

[0015] As the approach of a chemical treatment, the approach immersed in a chlorosulfonic acid, a sulfuric acid, an oleum, an oleum / phosphoric-acid triethyl complex in a base material filter is mentioned. When inside or a chlorosulfonic acid is used, since a sulfonyl chloride radical can be efficiently introduced into a base material filter also at low temperature, it is desirable. In order to control the fall on the strength accompanying the functional-group installation reaction of a base material although you may use as it is when using a chlorosulfonic acid, it is desirable to dilute and use it for 10 - 50 mass % extent with solvents, such as tetrachloroethane and trichloroethane.

[0016] a radiation graft pile -- making the monomer (collectively henceforth a functional-group installation

monomer) which can introduce the monomer or functional group containing a functional group into a base material filter immersed as an art depended lawfully, radiation irradiation is carried out, after carrying out graft polymerization and irradiating a radiation at a base material filter, a functional-group installation monomer may be made immersed and graft polymerization may be carried out. However, since handling is complicated, the latter approach of the approach of carrying out radiation irradiation is desirable [making a functional-group installation monomer immersed in a base material filter,].

[0017] a radiation graft pile -- the radiation treatment which can be set lawfully has the radiation treatment mentioned above and desirable processing of the same conditions. As for radiation irradiation here, it is still more desirable to carry out under reduced pressure or in inert gas ambient atmospheres, such as nitrogen, in order to protect the radical generated during an exposure. Moreover, in order to prevent the fall of radical concentration after irradiating a radiation until a base material is immersed in a functional-group installation monomer, it is desirable to hold a base material at low temperature. It is desirable to also perform immersion to the functional-group installation monomer of a base material under reduced pressure or in an inert gas ambient atmosphere, and the temperature of graft polymerization has desirable 40-90 degrees C.

[0018] As a functional-group installation monomer, styrene, alpha methyl styrene, chloro methyl styrene, Alkyl methacrylate, alkyl acrylate, acrylonitrile, An acrolein, glycidyl methacrylate, glycidyl acrylate, Vinyl acetate, a styrene sulfonic acid or its salt, an acrylic acid, or its salt, A methacrylic acid or its salt, a crotonic acid, an itaconic acid, 2-acrylamido-2-methyl propane sulfonic acid, A perfluoro sulfonyl fluoride, vinylbenzyl trimethylammonium chloride, Arylamine or its salt, 4-vinylpyridine, 2-vinylpyridine, 1-vinyl imidazole, 2-vinyl pyrazine, 4-(3-butenyl) pyridine, Acrylamide, N,N-dimethylacrylamide, N-(3-(N and N-dimethyl) aminopropyl) acrylamide, 2-(N and N-dimethylaminoethyl) acrylate, 2-hydroxyethyl acrylate, The compound which has 2-hydroxyethyl methacrylate, and a vinyl group and a sulfonic group, or its salt, The fluorine-containing compound which has the methoxycarbonyl group expressed with $\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2-\text{CF}(\text{CF}_3))_v-(\text{CF}_2)_w-\text{COOCH}_3$ grade (however, v and w are zero or more integers, and are not $v=w=0$.) etc. -- it is mentioned.

[0019] When it is a liquid, after the above-mentioned functional-group installation monomer may be immersed directly and dilutes a base material filter using a solvent, it may be immersed in a base material filter. Moreover, the approach of making a functional-group installation monomer a gas under reduced pressure, and introducing into a base material filter in addition to the approach immersed in a functional-group installation monomer in a base material filter, can also be adopted, and a gas can also be diluted with inert gas, such as nitrogen, in this case. When a functional-group installation monomer is a solid-state, it can be used making it dissolve in the solvent which a functional-group installation monomer dissolves.

[0020] The above-mentioned radiation treatment, electrodischarge treatment, a chemical treatment, and graft polymerization method processing may perform any one sort of processings, and may use together two or more sorts of processings.

[0021] As for the ion exchange capacity of the ion-exchange nature polymer used by this invention, it is desirable that they are 0.8 - 4.0 milliequivalent / g desiccation resin. Since the ion-exchange nature polymer used in order to fully remove the ionicity matter which is an impurity in gas will be needed in large quantities and equipment will become large if ion exchange capacity is smaller than 0.8 milliequivalent / g desiccation resin, it is not desirable. Moreover, if ion exchange capacity is larger than 4.0 milliequivalent / g desiccation resin, the reinforcement of an ion-exchange nature polymer will fall and breakage will tend to take place during processing. When ion exchange capacity is 1.0 - 3.0 milliequivalent / g desiccation resin, especially since there is also reinforcement of an ion-exchange nature polymer and gas can be processed efficiently, it is desirable.

[0022] In this invention, although the gas supplied to a fuel cell may be supplied since only a cation-exchange nature filter passes only an anion-exchange nature filter depending on an impurity, it is desirable to be supplied since both a cation-exchange nature filter and an anion-exchange nature filter are passed. What is necessary is to carry out the laminating of the cation-exchange nature filter produced in this case using the cation-exchange nature polymer, and the anion-exchange nature filter produced using the anion-exchange nature polymer, and just to make it a fuel cell supplied, after gas passes both ion-exchange nature filters.

[0023]

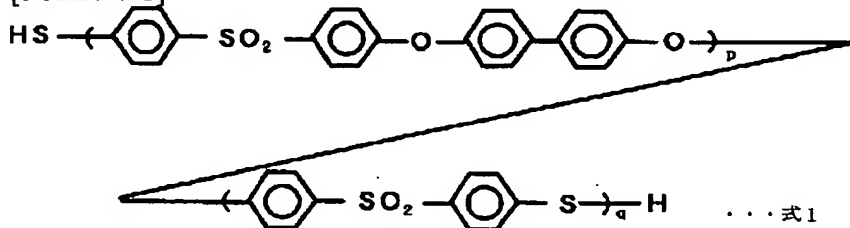
[Example] [Example 1] According to the synthesis method indicated by the example 11 of JP,61-168629,A, the polysulfone / poly thioether sulfone copolymer (henceforth Copolymer a) expressed with a formula 1 as is the following were obtained.

[0024] First, 3,6-mol bisphenol A, a sodium-hydroxide water solution and a N-methyl-2-pyrrolidone, and

toluene were taught to the autoclave, and nitrogen gas was heated with the sink, and water and toluene were removed and it cooled. Taught this 3.96-mol 4 and 4'-dichloro diphenylsulfone, it was made to react at 160 degrees C in nitrogen-gas-atmosphere mind for 3 hours, and the reactant which consists of a repeat unit of aromatic series polysulfone was obtained. Added 3.24 mols dichloro diphenylsulfone, the 3.78-mol sodium sulfide, and an acetic-anhydride lithium and a N-methyl-2-pyrrolidone to this, pressurized 0.49MPa(s) with nitrogen gas, it was made to react at 160 degrees C after cooling for 3 hours, and the 2200g copolymer a was obtained. In addition, in the formula 1, it was $p/q=1/1$, and the intrinsic viscosity of Copolymer a was 0.50. Moreover, the content of the aromatic series ring which has not been combined with $-SO_2-$ which is an electronic suction nature machine was 33-mol % in all the aromatic series ring of Copolymer a.

[0025]

[Formula 1]



[0026] Next, after dissolving the 750g copolymer a in the 1,1,2,2-tetrachloroethane of 10L, 4000g methane (chloro methoxy) and 45g anhydrous salt-sized tin were added, and the chloromethylation reaction was performed at 110 degrees C for 4 hours. Subsequently, after settling a resultant using methanol 50L, this resultant was washed and 850g (henceforth Copolymer b) of copolymers which chloromethylated Copolymer a was obtained. The rate of installation of the chloro methyl group in Copolymer b was about 1.9 per 1 repeat unit, and when the whole of this chloro methyl group was aminated by the trimethylamine, ion exchange capacity was 2.2 milliequivalent / g desiccation resin.

[0027] N.N-dimethylformamide solution 1140mL of the trimethylamine of one mol / L was dropped slowly, having dissolved the 500g copolymer b in 2830g N.N-dimethylformamide, and agitating the obtained solution at 0 degree C. Subsequently, 2-methoxyethanol 500g was added to this, and the solution of the anion-exchange polymer of ion-exchange-capacity 2.0 milliequivalent / g desiccation resin was obtained.

[0028] Moreover, two sorts of solutions of the solution which dissolved the 500g copolymer a in the 1,1,2-trichloroethane of 3350mL(s), and the solution which carried out dropping mixing of the 412g of the oleums 60% at 0 degree C at the mixed liquor of 281g phosphoric-acid triethyl and the 1,1,2-trichloroethane of 2000mL(s) were prepared, and two sorts of these solutions were dropped at 25 degrees C into 1,1,2-trichloroethane 3500mL. This was agitated for 100 hours and cation-exchange polymer 420g into which the deposit polymer was filtered, and it washed, dried and the sulfonic group was introduced was obtained. The rate of installation of the sulfonic group in the obtained polymer was about 1.5 per 1 repeat unit, and ion exchange capacity was 2.0 milliequivalent / g desiccation resin. Obtained polymer 400g was dissolved in 1600g of N-methyl-2-pyrrolidones, and the cation-exchange polymer solution was obtained.

[0029] Two things which performed at the exposure rate of 10 kGy/h for 5 hours, and performed gamma irradiation of 50kG(ies) in total under reduced pressure of the filter which consists of a polyethylene fiber of 500 micrometers in thickness and metsuke amount 200 g/m² were prepared, it immersed and dried in each above-mentioned solution, and the anion-exchange nature filter and the cation-exchange nature filter were produced. The thickness of the filter after desiccation was 510 micrometers and 530 micrometers, respectively, and metsuke amount reached 285 g/m² and there was 300 g/m². The sodium-hydroxide water solution of 0.1 mols / L was made immersed about an anion-exchange nature filter, and the counter ion considered as the quarternary-ammonium-salt radical of OH ion.

[0030] The cation-exchange nature filter and anion-exchange nature filter which were obtained are cut to discoid with a diameter of 10cm, respectively, two sheets are held in a filter holder in piles, it installs between the compressor which supplies the air by the side of a cathode, and a fuel cell cel, and that to which cathode side air passed this filter was supplied to the fuel cell cel.

[0031] A fuel cell cel is the following, and was made and assembled. The copolymer (ion-exchange-capacity 1.1 milliequivalent / g desiccation resin) and platinum support carbon which consist of a polymerization unit based on tetrafluoroethylene and a polymerization unit based on $CF_2=CF-OCF_2CF(CF_3)O(CF_2)_2SO_3H$ were included with the mass ratio of 1:3, and coating of the coating liquid which uses

ethanol as a solvent was carried out by the die coat method on the carbon cloth. The gas diffusion electrode with which this was dried and the gas diffusion electrode layer of 10 micrometers in thickness and amount of platinum support 0.5 mg/cm² was formed was produced.

[0032] Between the two above-mentioned gas diffusion electrodes, the cation exchange membrane (50 micrometers in thickness) which consists of a copolymer (ion-exchange-capacity 1.1 milliequivalent / g desiccation resin) which consists of a polymerization unit based on tetrafluoroethylene and a polymerization unit based on CF₂=CF-OCF₂CF(CF₃) O(CF₂)₂SO₃H was pinched, it pressed using the monotonous press machine, and the membrane electrode zygote was produced. On the outside of this membrane electrode zygote, the heater has been arranged on that outside to the charge collector made from titanium, the gas supply room of the product [outside / that] made from PTFE further, and the pan, and the fuel cell cel of 2 was assembled 9cm of effective film surface products.

[0033] The temperature of a fuel cell was kept at 80 degrees C, and hydrogen was supplied to the air and the anode which passed the filter to the cathode with two atmospheric pressures, respectively. Terminal voltage was 0.60V when the terminal voltage at the time of current density 1 A/cm² was measured. Furthermore, continuous running was performed for the above-mentioned fuel cell by 80 degrees C and current density 1 A/cm². The terminal voltage of 1000 hours after is 0.60V, and did not have the first stage and change.

[0034] [Example 2] After dissolving 500g (the Amoco [Corp.] make, a trade name: YUDERU P-1700) of copolymers of polysulfone in 1,1,2,2-tetrachloroethane 5200mL, the chloromethylation reaction was performed at the temperature of 50 degrees C for 0.5 hours, having added methane (chloro methoxy) 2350g and anhydrous salt-sized tin 45g, and carrying out a nitrogen purge. Subsequently, after settling a resultant in methanol 40L, this resultant was washed and 530g (henceforth Copolymer c) of chloromethylation copolymers was obtained. The rate of installation of the chloro methyl group in Copolymer c was about 0.9 pieces per 1 repeat, and when the whole of this chloro methyl group was aminated by the trimethylamine, ion exchange capacity was 1.7 milliequivalent / g desiccation resin.

[0035] The 500g copolymer c was dissolved in 2830g of N.N-dimethylformamide, and the 15 mass % solution was prepared. After 470mL(s) of the N.N-dimethylformamide solution of the trimethylamine of one mol / L were dropped slowly, agitating this solution at 0 degree C, 2-methoxyethanol 70g was added and ion exchange capacity obtained the anion-exchange nature polymer solution of 0.9 milliequivalent / g desiccation resin.

[0036] On the other hand, two mols tetrafluoroethylene and CF₂=CFOCF₂CF(CF₃) O(CF₂)₂SO₂F [0.45-mol] were copolymerized at 70 degrees C by having made azobisisobutyronitril into the initiator for 5 hours, and the copolymer of ion-exchange-capacity 1.1 milliequivalent / g desiccation resin was obtained. After hydrolyzing this over 16 hours at 90 degrees C in 20%KOH water solution, the cation-exchange nature polymer solution with which all solution mass contains the perfluorocarbon polymer which has a sulfonic group 9% was obtained by being immersed in the hydrochloric acid of one mol / L at a room temperature for 16 hours, changing SO₂F set into an acid type, and dissolving in the ethanol after rinsing desiccation.

[0037] Two things which carried out corona discharge treatment of the filter which consists of the thickness of 500 micrometers, metsuke amount of 200g/a polyethylene fiber of m2 by part for output [of 2kW] and processing speed/of 5m were prepared, and it was immersed in each above-mentioned solution, respectively, and it dried and the anion-exchange nature filter and the cation-exchange nature filter were produced. The thickness of the filter after desiccation was 530 micrometers and 540 micrometers, respectively, and metsuke amount was 300 g/m² and 310 g/m². 0.1 mols / L sodium-hydroxide water solution was made immersed about an anion-exchange nature filter, and the counter ion considered as the quarternary-ammonium-salt radical of OH ion.

[0038] It evaluated by assembling a fuel cell cel like Example 1. The temperature of a fuel cell was kept at 80 degrees C, and hydrogen was supplied to the air and the anode which passed the filter to the cathode with two atmospheric pressures, respectively. Terminal voltage was 0.58V when the terminal voltage at the time of current density 1 A/cm² was measured. Furthermore, continuous running was performed for the above-mentioned fuel cell cel by 80 degrees C and current density 1 A/cm². The terminal voltage of 1000 hours after is 0.58V, and did not have the first stage and change.

[0039] In the example 1 of [Example 3 (example of a comparison)], the fuel cell cel was assembled and evaluated like Example 1 except having set two sheets in piles, without processing the filter made from a polyethylene fiber to a filter holder. Terminal voltage was 0.60V when the terminal voltage at the time of current density 1 A/cm² was measured. However, the terminal voltage after 1000-hour operation fell to 0.51V.

[0040] In the example 2 of [Example 4 (example of a comparison)], it immersed and dried in each ion-exchange nature polymer solution, without carrying out corona discharge treatment of the filter made from a polyethylene fiber, and the anion-exchange nature filter and the cation-exchange nature filter were produced. The thickness of the filter after desiccation was 530 micrometers and 540 micrometers, respectively, and metsuke amount reached 300 g/m² and there was 310 g/m². The sodium-hydroxide water solution of 0.1 mols / L was made immersed about an anion-exchange nature filter, and the counter ion considered as the quarternary-ammonium-salt radical of OH ion. The fuel cell cel was similarly assembled and evaluated except having set in piles the filter obtained by the filter holder like Example 2 two sheets. Terminal voltage was 0.59V when the terminal voltage at the time of current density 1 A/cm² was measured. However, the terminal voltage after 1000-hour operation fell to 0.53V.

[0041]

[Effect of the Invention] In this invention, since the gas processed with the ion-exchange nature filter which is excellent in endurance, i.e., the gas by which the ion component was removed, is supplied to the polymer electrolyte fuel cell, are recording of the ion into the solid-state polyelectrolyte film is lost. Therefore, even if it operates a fuel cell for a long period of time, the rise of resistance can be controlled and the fall of a generation-of-electrical-energy electrical potential difference can be controlled.

[Translation done.]